Low Cost Efficient Treatment for Contaminated Water

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Abstract

Heavy metals pose a risk of contaminating groundwater and surface water sources due to geogenic activities, industries and agricultural sources. The removal of heavy metals e.g., cadmium, lead, and zinc from drinking, industrial and irrigation water at low concentrations is a recurring challenge, especially in developing countries. Biosorption is a relatively new process that has proved to be very promising for removal of heavy metals from aqueous solutions. The removal of contaminants viz., Cd(II), Pb(II) and Zn(II) by rice husk (lignin containing material) was studied in the laboratory. Batch studies were performed to evaluate the influences of various experimental parameters like pH, initial concentration of metal ions, biosorbent dosage and contact time. The selectivity of the process is also studied. The findings show the efficiency of material for the removal these contaminants with a low concentration in the range 1-5 mg/L. The removal efficiency is up to 95%.

Keywords

biosorption; developing countries; heavy metals; low concentration; rice husk

INTRODUCTION

Due to development in technology, environmental pollution is one of the most important contemporary problems. Industries have a great potential to cause lake, streams, river and sea pollution. Ever increasing industrialization has led to increased disposal of heavy metals into the environment. Heavy metals contamination exists in aqueous waste streams of many industries, such as metal finishing, electroplating, metallurgical work, mining, chemical manufacturing, pesticides, fertilizers, dyes, pigments, tanning and battery manufacturing (KANG et al. 2007; LESMANA et al. 2009). Heavy metals are reported as priority pollutants, due to their mobility in natural water ecosystems. Their presence has brought severe environmental problems due to their toxicity even at low concentrations and insusceptibility to the environment. These heavy metals are not biodegradable and tend to in living organisms, causing various diseases and disorders. For instance, cadmium exposes human health to severe risks, as it can aggravate cancer, bone damage, vomiting, diarrhea, kidney damage, mucous membrane destruction, itai-itai disease, and affect the production of progesterone and testosterone (GODT et al. 2006). On the other hand, lead has been as one of the three most toxic heavy metals that have dormant longterm negative impacts on health, causing hepatitis, anemia, nephritic syndrome brain damage, mental deficiency, anorexia, vomiting, malaise and encephalopathy (DENG et al. 2006). Also, zinc poisoning can lead to nausea, vomiting, loss of appetite, abdominal cramps, diarrhea, and headaches, anemia, damage the pancreas, and decrease levels of high-density lipoprotein (HDL) cholesterol (FNB, 2001).

Conventional methods for heavy metal removal from water include ion exchange, reduction, precipitation, evaporation, electrochemical treatment, membrane filtration, reverse osmosis, electrodialysis and carbon adsorption. Most of these methods may be expensive or ineffective when metals are dissolved at relatively low concentrations (VOLESKY 1990; RORRER 1998). Adsorption has been proved to be an excellent way to treat contaminated water, offering significant advantages like the low-cost, greater availability, profitability, easiness of operation, effectiveness in reducing the concentration of heavy metal ions to very low levels (DEMIRBAS 2008). Cost considerations can make it expedient to use local materials, produced in agricultural or industrial operations, as adsorbents for these toxics. Adsorption process is recommended for the removal of low concentrations of metal ions in water. This process implies the presence of an "adsorbent" solid that binds molecules by physical attractive forces, ion exchange, and chemical binding. Activated carbon is most popular and widely used adsorbent for heavy metal removal in water treatment applications throughout the world. Though it's prolific use, it remains an expensive material as its cost increase with the quality (BABEL and KURNIAWAN 2003). Complexing agents are required to improve its removal performance for inorganic matters.
Biosorption is a relatively new process that has proven very promising for removal of heavy metals from aqueous solutions. Low-cost agricultural/plant wastes can be used as adsorbent materials for effective removal and recovery of heavy metals from water (KRATOCHVIL and VOLESKY 1998; BASSO et al., 2002). The major advantages of biosorption over conventional methods are easy of operation, high efficiency, low-cost, availability, profitability, waste reuse, minimization of chemical and/or biological sludge, regeneration of biosorbent, no additional nutrient requirement, eco-friendly and possibility of metal recovery (AHALYA et al. 2003). Metal biosorption is a complex process affected by several factors. Mechanisms involved in the biosorption process include chemisorptions, complexation, adsorption-complexation on surface and pores, microprecipitation, ion exchange, chelation, heavy metal hydroxide condensation onto biosurface, and surface adsorption (GARDEA-TORRESDEY et al. 2004; VOLESKY 2001).

Agricultural waste materials are usually generated in large quantities. Rice husk, a major by-product of the rice milling industry, is one of the most commonly available lignocellulosic materials. The annual rice husk produce in India amounts is generally approximately 120 million tons. Rice husk is typically composed of 20% ash, 38% cellulose, 22% lignin, 18% pentose, and 2% other organic components (JAMES and RAO 1986). Lignin is a natural amorphous cross-linked resin that has an aromatic three-dimensional polymer structure containing a number of functional groups such as phenolic, hydroxyl, carboxyl, benzyl alcohol, methoxyl, and aldehyde groups (SARKANEN and LUDWIG 1971), making it potentially useful as an adsorbent material for removal of heavy metals from water. Lignin consists of high quantity of phenolic units and carboxyl groups which have higher affinity for heavy metal ions. There are no beneficial uses for this type of residue and its disposal constituents a major problem (OLIVEIRA et al. 2008). In addition, as sustainable development should be prioritized, the development of techniques for giving extra value and reusing this type of residue should be sought.

Thus, the objective of this study was to investigate the feasibility of using natural rice husk as biosorbents for the removal of cadmium, lead and zinc metal ions from synthetic aqueous media.

MATERIAL & METHODS

Adsorption experiments of the heavy metal ions: Cd, Pb and Zn onto rice husk were performed in the batch mode from synthetic solutions. Cadmium, zinc and lead are metallic elements with high atomic weights which can damage living things at low concentrations and tend to accumulate in the food chain.

Adsorbent

Rice husk were obtained from the local rice mill. The husks were dried in sunlight for one week, and then crushed and sieved to get particle size less than 1.5 mm. With the exception of crushing and sieving, the rice husks were not pretreated prior to the adsorption experiments. The dried biomass was designated as the Natural Rice Husk (NRH).

Chemicals

Analytical grade of cadmium nitrate $Cd(NO_3)_2$, lead nitrate $Pb(NO_3)_2$ and zinc nitrate $Zn(NO_3)_2$ were obtained from Fisher Scientific. All the solutions were used as the standard stock solutions for the metal ions source. The concentration of stock solutions was at 1000 ppm. Lower concentrations were then prepared when required by further dilution of the stock solution with distilled water. The mixtures of chosen Me^{2+} were made to get 1, 3 and 5 ppm concentration of each metal ion solution. Nitric acid and sodium hydroxide obtained from Aldrich Chemical Company were used for pH adjustment when the effect of this variable was investigated.

Instrumentation

Spectro Genesis Inductively Coupled Plasma (ICP) Spectrometer was used to analyze the concentrations of cadmium, lead and zinc metal ions. The nebulizer type used in the instrument for analysis is Bergner. The instrument operates on argon created plasma. The detection limits of the instruments are equal to or below the recommended EPA limits for measured metal ions. The pHTestr30 was used for the pH analysis of samples. An Orion stirring plate was used to stir the samples. The circulation was set to 80 cycles per minute.

Experimental procedure

The experiments were performed in a batch process in a series of beakers equipped with magnetic stirrers by stirring 2 g of the NRH with 50 mL of mixed metal ions solution with a known, previously determined, initial concentration of the considered metal ions and the required pH value. At the end of predetermined time, the suspension was filtered and the remaining concentration of metal ions in the aqueous phase was determined. The removal efficiency (RE) was then calculated from experimental data using the following relationship:
$RE\% = (C_i – C_f) * 100 / C_i$,

Where, C_i and C_f are initial and final concentrations of metal ions.

The following parameters of the processes were changed and studied during these experiments: adsorption time, influence of initial pH, biosorbent dosage and initial concentration of metal ions. All the experiments were performed at ambient temperature. Blanks were run in parallel in all the experiments. All the experiments were carried out in duplicate and the average values are reported.

RESULTS AND DISCUSSION

Effect of adsorption time

The effect of time on the sorption of metal ions by NRH was studied by taking 2 g adsorbent with 50mL of mixed metal ions solution having 1ppm concentration of each metal ion. The flasks were shaken for different time intervals (10-120 min) in a temperature controlled shaker. The findings on the sorption of metal ions are shown in Fig. 1. The results show that the sorption increased with time of equilibrium and it became almost constant at 100 min for all metal ions. The changes in the metal ions uptake may be due to the fact that all active sites of adsorbent were vacant and the solute concentration was high at the beginning. After that, only a very low increase in the metal ions uptake was seen as there are few surface active sites on the adsorbent. The quick equilibrium time is due to the small particle size as the effective surface area is high for small particles (XUAN 2006).

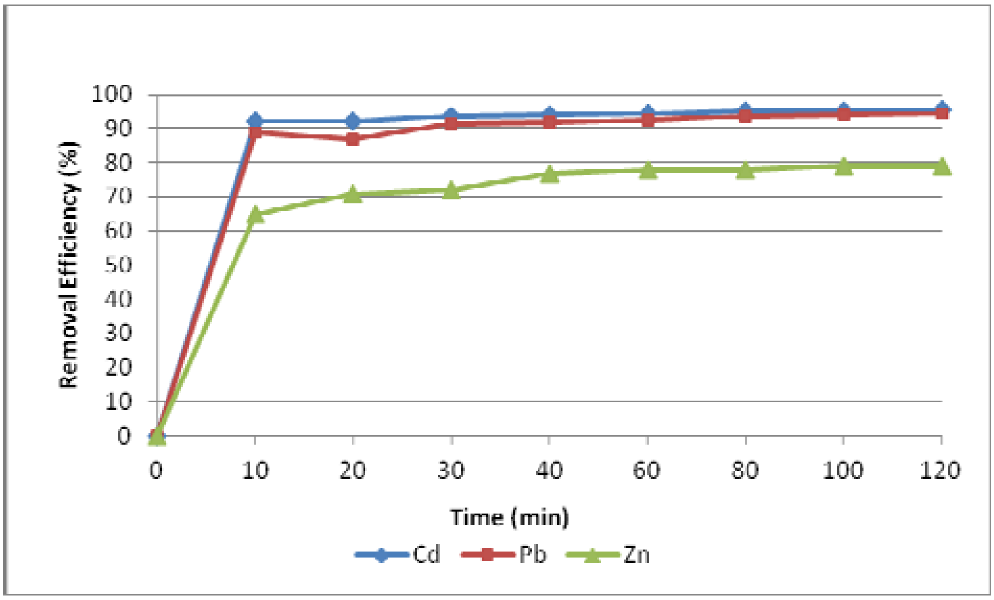


Fig. 1. Effect of equilibrium time on the sorption of Cd(II), Pb(II) and Zn(II) on NRH. (volume of solution = 50mL, biosorbent dosage = 2 g, concentration of each metal ions = 1 ppm , pH = 8)

Effect of initial pH

The pH of the aqueous solution is a main controlling parameter in the adsorption process (AJMAL et al. 1998). This is mostly due to the fact that protons are the main competing adsorbate ions and partly due to the fact that the pH of a solution influences the chemical speciation of the metal ions in the solution and the ionization of the functional groups of the adsorbents (BOZIC et al. 2009). Fig. 2. presents the effect of pH on the adsorption the metal ions in the experiments carried out at different pH values. It can be observed that the adsorption capacity of the metal ions by NRH is clearly affected by the pH. The dependence of metal uptake on pH may be related to the functional groups of the adsorbent and/or the solution chemistry. The minimal adsorption at low pH may be due to the higher concentrations and high mobility of protons, which acted as a competitor and preferentially adsorbed rather than the metal ions on the active binding sites (ANNADURAI et al. 2002). Natural nut basically consists of lignin. Lignin contains two major types of functional groups that have strong interactions with heavy metal ions: carboxylic and phenolic groups (RAVAT et al., 2000; BOUANDA et al., 2002).

These groups might be responsible for the efficient adsorption of all three heavy metal ions in the wide range of pH 2.5 – 10.

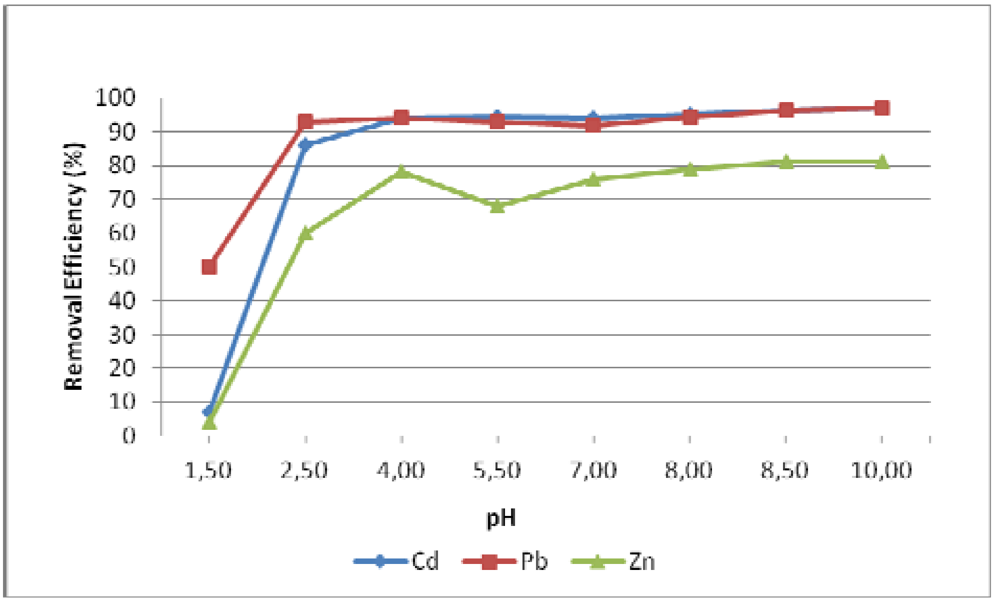


Fig. 2. The effect of initial pH on the sorption of Cd(II), Pb(II) and Zn(II) on NRH. (volume of solution = 50mL, biosorbent dosage = 2 g, concentration of each metal ions = 1 ppm, time = 100 min)

Effect of biosorbent dosage

Fig. 3 shows the effect of biosorbent dosage on the amount of the metal ions adsorbed. It is clear that the amount of zinc metal ions adsorbed varied with the biosorbent quantity and adsorption increases with an increase in biosorbent dosage. This can be easily explained by an increase in surface area (i.e. due to more availability of active adsorption sites) with an increase in biosorbent dosage. Several factors affecting adsorption are number of sites in the biosorbent material, the accessibility of the sites, the chemical state of sites (i.e., availability) and the affinity between the site and the metal (i.e., binding strength). Similar behavior for the effect of biosorbent dosage on metal adsorption was observed in the literature for a variety of adsorbents (AGRAWAL et al. 2004). The effect of increasing biosorbent dosage on the adsorption of cadmium and lead ions was not significant, presenting only slight change with an increase in biosorbent dosage.

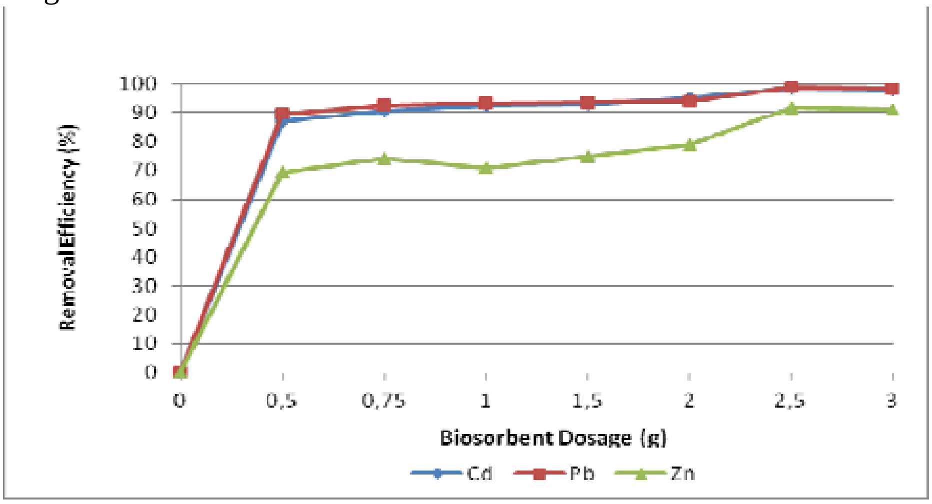
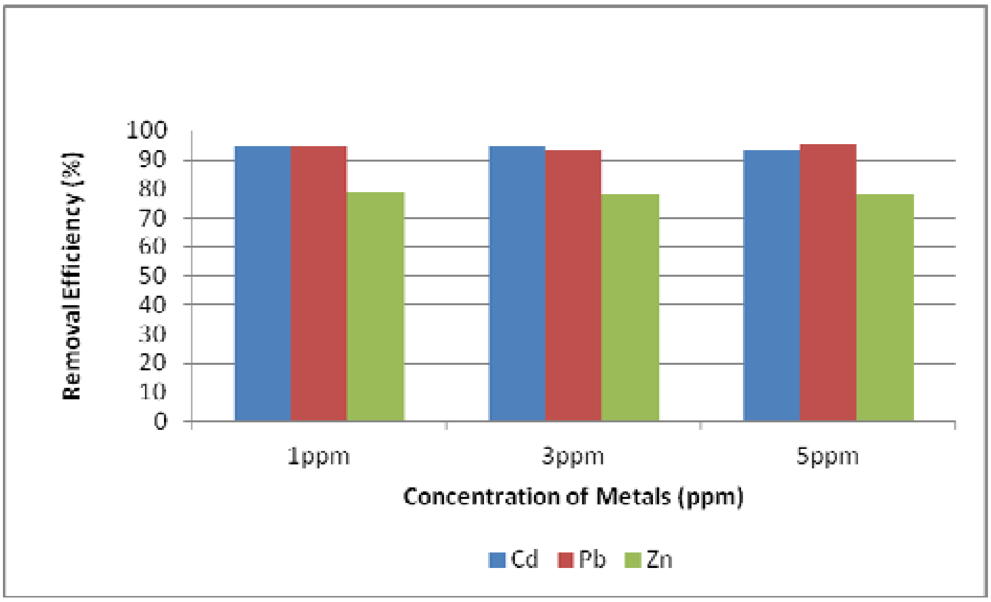


Fig. 3. The effect of biosorbent dosage on the sorption of Cd(II), Pb(II) and Zn(II) on NRH. (volume of solution = 50mL, concentration of each metal ions = 1 ppm, pH = 8, time = 100 min)

Effect of initial concentration of metal ions

The effect of initial concentration of ions in the aqueous phase is an important parameter in the adsorption process. Some studies observed that with an increase in the initial concentration of metal ions, the corresponding adsorption capacity is shifted towards higher values i.e. with increasing the initial concentration the rate increased proportionally (YU et al. 2000). In this study, the effect of initial concentration of metal ions does not show a specific trend.



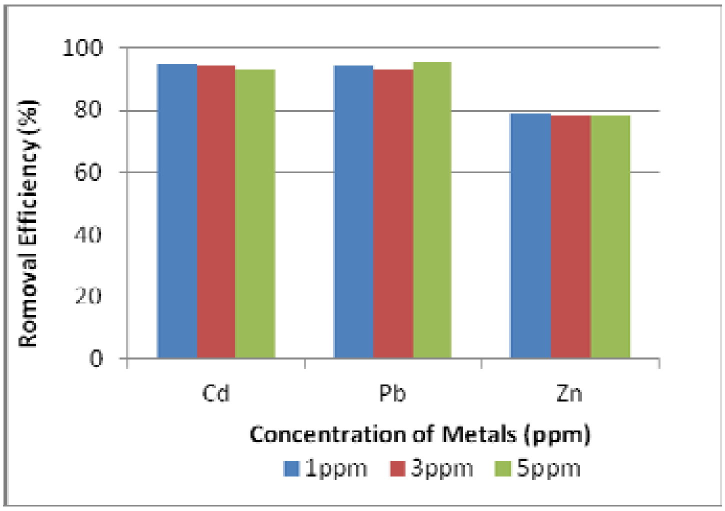


Fig. 4. (a and b) The effect of initial metal ions concentration on the sorption of Cd(II), Pb(II) and Zn(II) on NRH. (volume of solution = 50mL, quantity of material = 2 g, pH = 8, time = 100 min)

Effect of ion species on the adsorption – selectivity of the process

From the engineering point of view, it is significant to obtain evidence concerning the ability of the adsorbent to adsorb different heavy metal ions. The removal efficiency at the plateau values differ for different ions, showing evidence about the adsorption ability of the adsorbent which can be achieved for each of the measured metal ion species. From the study of above parameters, it is clear that the highest adsorption ability was for cadmium, lead and then zinc i.e. ranking the adsorption ability of the measured metal ions, the following series is obtained: Cd(II)>Pb(II)>Zn(II).

CONCLUSIONS

There has been an increasing interest in using natural biosorbents for the adsorption of heavy metal ions. A feasibility study of using rice husk as untreated biosorbents for the removal of heavy metal ions from aqueous solution was successfully carried out. The results obtained in this study show that natural rice husks can be considered as a potential biosorbent for the removal of cadmium, lead and zinc metal ions. The adsorption of metal ions is strongly dependent on the adsorption time, initial pH of the solution, biosorbent dosage and initial concentration of metal ions. The adsorption kinetics is fast and the system is almost at equilibrium at 100 min of contact time. The maximum uptake of metal ions was found at pH values in between 2.5 and 10, showing wide range of fitness of pH for adsorption. Acidification of the aqueous phase leads to decrease in biosorption capacity of NRH due to increase in proton concentration which occupied active site of biosorbent. An increase in biosorbent dosage in the suspension leads an increase in the adsorption degree due to more number of active sites available to adsorb metal ions. The increase in the initial concentration of metal ions did not show a specific trend like an increase in adsorption degree proportionally. Ranking the adsorption ability of the measured metal ions, the following series is obtained: Cd(II)>Pb(II)>Zn(II). It is an effective biosorbent for the removal of cadmium, lead and zinc metal ions from water.

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